

Photocatalytic oxidation mechanism of arsenite on tungsten trioxide under visible light



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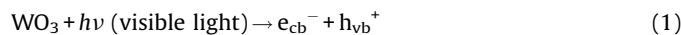
ABSTRACT

The oxidation of arsenite (As(III)) to arsenate (As(V)) and the involved oxidants on tungsten trioxide (WO₃) under visible light were mechanically investigated. Three oxidant species, valence-band hole (h_{vb}⁺), hydrogen peroxide (H₂O₂), and hydroxyl radical (•OH), can be generated on WO₃ under visible light. However, As(III) was not oxidized to As(V) in the presence of H₂O₂. In addition, the oxidation rate of As(III) to As(V) was not reduced in the presence of •OH scavenger. These results indicate that the oxidation of As(III) to As(V) is primarily initiated by hole, but both •OH and H₂O₂ are little involved in As(III) oxidation to As(V). This hole-mediated oxidation of As(III) to As(V) on WO₃ was further confirmed by X-ray photoelectron spectroscopy (XPS) analysis (i.e., the adsorption of As(III) on WO₃) and photoelectrochemical measurement (i.e., the enhanced photocurrent by As(III) addition). Although •OH is little involved in As(III) oxidation to As(V), the production of •OH was reduced in the presence of As(III). This behavior implies that As(III) on WO₃ acts as an external charge recombination center, where the oxidation of As(III) to intermediate As(IV) species by hole or •OH is immediately followed by the reduction of As(IV) to As(III) by conduction-band electron (e_{cb}⁻). Therefore, the direct oxidation of As(III) to As(V) by two-hole transfer can be proposed as the primary oxidation pathway of As(III) to As(V) on WO₃ under visible light.

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1. Introduction

Tungsten trioxide (WO₃) has been extensively studied as a viable environmental photocatalyst because it is active under visible light, stable, and non-toxic [1–5]. The photocatalytic reactions on WO₃ can be initiated by absorbing visible-light photons, which create conduction-band electrons (e_{cb}⁻, reductant) and valence-band holes (h_{vb}⁺, oxidant) (Reaction (1)). Subsequently, hydrogen peroxide (H₂O₂) and hydroxyl radical (•OH) as an oxidant are primarily generated through the two-electron reduction of dioxygen and one-electron reduction of H₂O₂, respectively (Reactions (2) and (3)) [6–8].



Unlike titanium dioxide (TiO₂, the most popular photocatalyst), the formation of superoxide/hydroperoxyl radical (O₂^{•-}/HO₂[•]) as an oxidant is limited on WO₃ because the conduction-band (CB) position of WO₃ (+0.3–0.5 V_{NHE} [9–11]) is more positive than the one-electron reduction potential of dioxygen [E⁰(O₂/O₂^{•-}) = -0.33 V_{NHE} and E⁰(O₂/HO₂[•]) = -0.05 V_{NHE} [12]]. The one-electron transfer from WO₃ CB to dioxygen (i.e., the formation of O₂^{•-}/HO₂[•]) is not thermodynamically favored. Therefore, three oxidants except O₂^{•-}/HO₂[•] (hole, H₂O₂, and •OH) can be involved in the oxidative degradation processes on WO₃.

Arsenic (As) pollution can occur not only from anthropogenic sources (e.g., discharge of industrial and agricultural wastewaters containing arsenic) but also from natural sources (e.g., natural weathering and dissolution of arsenic-bearing minerals) [13–15]. Arsenic mainly exists as arsenite (As(III)) and arsenate (As(V)) in water, and its oxidation state critically affects the toxicity, mobility, and removal efficiency in physical treatment processes (e.g., adsorption, coagulation, and precipitation) [16]. As(III) is more toxic, mobile, and difficult to remove using physical treatment processes than As(V), which requires the pre-oxidation of As(III) to

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As(V) [17]. In this regard, various pre-oxidation methods have been developed and used to reduce the toxicity and enhance the immobilization of arsenic; they include photocatalysis [18,19], electrocatalysis [20,21], chemical process [22,23], and biological process [24,25].

Among these pre-oxidation methods, photocatalysis is a practical candidate for As(III) oxidation because of its high efficiency, no requirement for chemical oxidants and electrical energy, and applicability at a broad range of As(III) concentrations. The understanding of photocatalytic As(III) oxidation mechanism provides useful information on the synthesis and surface modification of photocatalyst and the establishment of operating conditions for efficient photocatalytic As(III) oxidation. Although the photocatalytic oxidation mechanism of As(III) and the involved oxidants on TiO₂ (the most popular UV light photocatalyst) have been extensively studied [26–29], that on WO₃ (the most popular visible light photocatalyst) have been hardly explored. The photocatalytic oxidation mechanism of As(III) on TiO₂ should be different from that on WO₃ because the surface properties, oxidant species, band positions, and light absorption range are different from each other. Therefore, the As(III) oxidation mechanism on WO₃ should be independently studied to use WO₃ as a photocatalyst more efficiently in the photocatalytic As(III) oxidation process.

In this study, we investigated the oxidation mechanism of As(III) to As(V) and the involved oxidants on WO₃ under visible light by investigating the effect of •OH scavenger on As(III) oxidation to As(V) and As(III) on •OH production. In addition, surface analysis and photoelectrochemical measurement were performed to support the hole-mediated As(III) oxidation pathway.

2. Experimental

2.1. Materials and chemicals

Materials and chemicals were used as received without further purification. They include tungsten trioxide (WO₃, nanopowder, <100 nm particle size (BET), Aldrich), NaAsO₂ (As(III), Aldrich), Na₂HAsO₄·7H₂O (As(V), Sigma), hydrogen peroxide (H₂O₂, Aldrich), *tert*-butyl alcohol (TBA, Shinyo), coumarin (CM, Aldrich), benzoic acid (BA, Aldrich), 4-hydroxybenzoic acid (4-HBA, Aldrich), molybdate reagent solution [the mixture of hexaammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, 0.02 M), sulfuric acid (H₂SO₄, 0.56 M), and potassium antimony(III) oxide tartrate hemihydrate (K(SbO)C₄H₄O₆·0.5H₂O, 2.1 mM)] (Fluka), ascorbic acid (Junsei), dichloroacetate (DCA, Aldrich), and LiClO₄ (Aldrich). Deionized water was ultrapure (18.3 MΩ cm) and prepared using a Human-Power I+water purification system (Human corporation).

2.2. Photocatalytic experiments

WO₃ nanopowder (15 mg) was dispersed in deionized water by sonication for 1 min in an ultrasonic cleaning bath. An aliquot of the chemical stock solution was subsequently added to the suspension to yield the desired initial concentration (0.3 mL of 10 mM As(III) for [As(III)] = 100 μM, 15 mL of 20 mM BA for [BA] = 10 mM, 5 mL of 6 mM CM for [CM] = 1 mM, and 0.285 mL of 10.6 M TBA for [TBA] = 0.1 M). The total volume of solution was 30 mL. The initial pH (pH_i) of the suspension was adjusted to 3.0 using a HClO₄ solution; then, the suspension was stirred for 30 min to allow the adsorption equilibrium of As(III) on the surface of WO₃ in the dark.

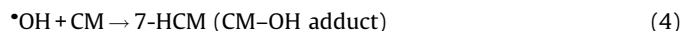
A 300 W Xe arc lamp (Oriel) was used as a light source. The light beam was passed through a 5 cm IR water filter and a cutoff filter (λ > 420 nm) and focused onto a cylindrical Pyrex reactor (volume = 55.5 mL and diameter = 3.5 cm) that contained WO₃, coumarin

(CM) (or benzoic acid (BA) or *tert*-butyl alcohol (TBA)), and As(III). The incident light intensity was measured by using ferrioxalate actinometry [30] and estimated to be about 0.82 × 10⁻³ einstein min⁻¹ L⁻¹. The reactor was open to ambient air to prevent the depletion of dissolved dioxygen, and magnetically stirred during the visible-light irradiation.

2.3. Chemical and surface analyses

Sample aliquots were withdrawn from the reactor intermittently during the visible-light irradiation and filtered through a 0.45 μm PTFE syringe filter (Millipore) to remove WO₃ particles.

The production of •OH was monitored by measuring the fluorescence emission intensity of 7-hydroxycoumarin (7-HCM, CM-OH adduct) and the concentration of 4-hydroxybenzoic acid (4-HBA, BA-OH adduct), which were generated from Reactions (4) and (5), respectively [31,32].



The fluorescence emission intensity of 7-HCM was measured at 460 nm using a spectrofluorometer (Shimadzu RF-5301). Monochromatic light with a wavelength of 332 nm was used as the excitation source. The concentration of 4-HBA was quantified by comparing the chromatography peak area of the samples with that of the authentic standard at the identical retention time using a high-performance liquid chromatography (HPLC, Agilent 1100). The concentration of BA was also measured using HPLC analysis.

The concentration of As(V), which was generated from As(III) oxidation, was measured using the molybdenum blue method [33]. For the molybdenum blue method, 100 μL of ascorbic acid (0.5 M) and 200 μL of molybdate reagent solution were added to a diluted sample (0.5 mL of sample and 2.2 mL of deionized water). After 1 h, the absorbance of solution was measured at 870 nm (ε = 19,550 M⁻¹ cm⁻¹ [34]) using a UV-vis spectrophotometer (Shimadzu UV-2600).

X-ray photoelectron spectroscopy (XPS) analysis was performed using monochromatic Al Kα line (1486.6 eV) as an X-ray source (VG scientific ESCALAB 250).

2.4. Photoelectrochemical measurements

Photoelectrochemical measurements were performed using a conventional three-electrode system in the presence of LiClO₄ (0.1 M) as a background electrolyte. The WO₃-coated fluorine-doped SnO₂ (FTO, Pilkington) electrode, a graphite rod, and a saturated calomel electrode (SCE) were used as the working electrode, counter electrode, and reference electrode, respectively. WO₃ was coated on FTO using the doctor-blade method with Carbowax as a binder [35]. To remove the dissolved oxygen in the electrolyte (9 mL), argon was purged for 30 min prior to visible-light irradiation and continuously purged during the photocurrent (*I*_{ph}) measurement. *I*_{ph} was recorded using a computer-controlled potentiostat (Gamry Reference 600) under an applied potential of +0.5 V_{SCE} at the working electrode.

3. Results and discussion

3.1. Primary oxidant for As(III) oxidation on WO₃

Three oxidants (hole, H₂O₂, and •OH) can be generated in the visible-light irradiated suspension of WO₃; therefore, they are likely to be involved in the oxidation of As(III) to As(V). First, the

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